

## Determination of Potassium in River Water by Solvent Extraction-Flow Injection Analysis

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Potassium ions are hardly extractable into organic solvents because of their highly ionic property. However, crown ether-complexed potassium ions can be extracted into many organic solvents as ion-pairs when bulky dye anions are used as the counter ions. Thus, many extraction-spectrophotometric methods for potassium have been proposed based on such a strategy.<sup>1-6</sup> Dibenzo-18-crown-6 and 18-crown-6 are preferred because of their selective complex forming ability for potassium. This paper describes that flow injection analysis using dibenzo-18-crown-6 and the dichloro derivative of tropaeolin OO (TOOCl<sub>2</sub>: 4-[[4-(phenylamino)phenyl]azo]-2,5-dichlorobenzenesul-

fonic acid) is successful for the determination of potassium.

### Experimental

A diagram of the extraction-flow injection system is shown in Fig. 1. Distilled water, an aqueous solution containing TOOCl<sub>2</sub> ( $5 \times 10^{-4}$  mol dm<sup>-3</sup>), lithium hydroxide ( $3 \times 10^{-3}$  mol dm<sup>-3</sup>), and Li<sub>2</sub>EDTA ( $10^{-3}$  mol dm<sup>-3</sup>), and a benzene solution of dibenzo-18-crown-6 (DB18C6,  $4 \times 10^{-3}$  mol dm<sup>-3</sup>) were pumped individually with double plunger pumps (Sanuki Kogyo) at a flow rate of 0.8 cm<sup>3</sup> min<sup>-1</sup>. A sample solution (100 μl) was introduced into the flow system by using a six-port sample injection valve. A 0.5 mm bore PTFE tubing and PTFE fittings were used. At the mixing point of the aqueous and organic phases, a T-shaped segmentor was used to obtain a regular pattern of the alternate aqueous and benzene segments. In a phase separator, a porous PTFE membrane sheet (pore size: 0.8 μm) was used for the separation of both phases. The absorbance of the benzene phase separated was monitored with a spectrophotometer at 430 nm. Insoluble materials were removed prior to use from the TOOCl<sub>2</sub> and DB18C6 solutions by using membrane and cellulose filters, respectively.

### Results and Discussion

The extractability of potassium (measured by the peak height) increased as the coil length increased from 0.3 to 1 m but showed virtually no increase over the coil length range 1-3 m. A 1-m extraction coil (0.5 mm bore) was chosen.

The effect of the flow rate was examined in the range of 0.4 to 1.0 cm<sup>3</sup> min<sup>-1</sup>; the three solutions were always delivered at the same flow rate. The peak height gradually increased with an increase in the flow rate until a flow rate of 0.8 cm<sup>3</sup> min<sup>-1</sup> was reached. No appreciable increase was observed by the further

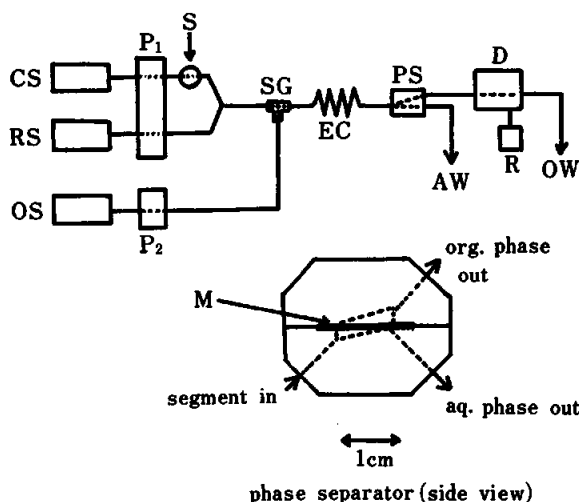


Fig. 1 Schematic diagram of extraction-flow injection system. CS, H<sub>2</sub>O; RS, aq. TOOCl<sub>2</sub> (LiOH+Li<sub>2</sub>EDTA) soln.; OS, DB18C6 benzene soln.; P<sub>1</sub>, P<sub>2</sub>, pumps (0.8 cm<sup>3</sup> min<sup>-1</sup>); S, sample injection port (100 μl); SG, segmentor; EC, extraction coil (0.5 mm×1 m); PS, phase separator; D, spectrophotometric detector (430 μm); R, recorder; AW, aqueous phase waste; OW, organic phase waste; M, PTFE membrane filter (0.8 μm).

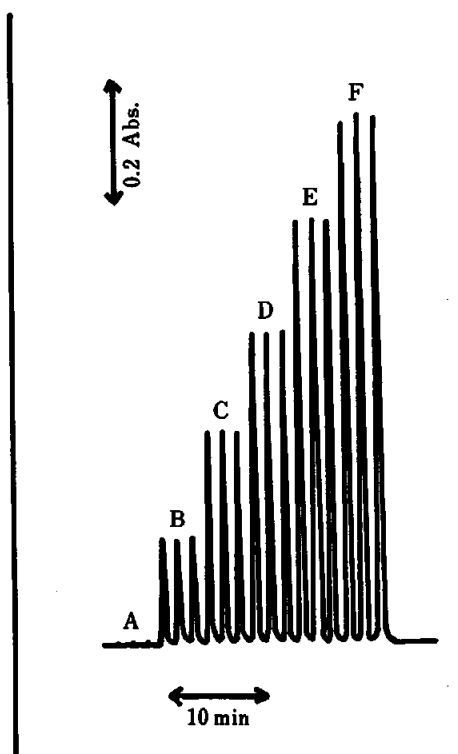


Fig. 2 Flow signals for the calibration curve of potassium.  $[K^+] \times 10^5 / \text{mol dm}^{-3}$ ; A, 0; B, 2; C, 4; D, 6; E, 8; F, 10.

increase of the flow rate. The peak width, on the other hand, gradually decreased with an increase in the flow rate. Accordingly, the three solutions were delivered at a flow rate of  $0.8 \text{ cm}^3 \text{ min}^{-1}$ .

A relation between the peak height and the potassium concentration was investigated by varying the concentration of DB18C6 from  $2 \times 10^{-3}$  to  $8 \times 10^{-3} \text{ mol dm}^{-3}$ . The peak height increased with an increase in the DB18C6 concentration. However, the linearity of the curves obtained was lost when the concentrations of DB18C6 above  $8 \times 10^{-3} \text{ mol dm}^{-3}$  were used. A concentration of  $4 \times 10^{-3} \text{ mol dm}^{-3}$  was chosen so as to attain the necessary sensitivity and linearity.

$\text{TOOCl}_2$  is slightly soluble in water. When concentrated  $\text{TOOCl}_2$  solutions ( $7 \times 10^{-4} \text{ mol dm}^{-4}$ ) come into contact with the organic solvent,  $\text{TOOCl}_2$  is liable to precipitate at the interface. The adsorption of the precipitates on the porous PTFE membrane sheet in the phase separator gave noisy baselines. A concentration of  $5 \times 10^{-4} \text{ mol dm}^{-3}$ , therefore, was selected for the  $\text{TOOCl}_2$  solution.

Figure 2 shows that the flow signals for potassium are well reproducible under such optimized conditions. The calibration curve was linear up to  $10^{-4} \text{ mol dm}^{-3}$  of potassium.

The effect of foreign ions was investigated. The results are summarized in Table 1.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and

Table 1 Effect of foreign ions

Ion	Concentration/ $\text{mol dm}^{-3}$	Peak height ratio
None <sup>a</sup>		1.00
$\text{Ca}^{2+}$	$5 \times 10^{-4}$	1.02
$\text{Mg}^{2+}$	$5 \times 10^{-4}$	1.03
$\text{Fe}^{3+}$	$5 \times 10^{-4}$	1.02
$\text{Na}^+$	$1 \times 10^{-3}$	1.07

a.  $K^+$ :  $5 \times 10^{-5} \text{ mol dm}^{-3}$ .

Table 2 Potassium in river waters

Water		Potassium, ppm	
		Proposed method	AAS <sup>a</sup>
Asahi river	A	1.34	1.29
	B	1.26	1.21
Yoshii river	A	1.52	1.52
	B	1.41	1.41
Takahashi river	A	1.15	1.18
	B	1.13	1.11

a. Atomic absorption method.

$\text{Fe}^{3+}$  ( $< 5 \times 10^{-4} \text{ mol dm}^{-3}$ ) showed virtually no interference but a large quantity of  $\text{Na}^+$  slightly interfered.

The analytical results of potassium in river waters are listed in Table 2. The potassium concentrations determined by the proposed method are in good agreement with those obtained by an atomic absorption method. The proposed flow injection analysis was less subject to interference from  $\text{Na}^+$  as compared with a batchwise method using the same analytical reagents.<sup>6</sup>

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